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Germylene complexes of tungsten pentacarbonyls $W(CO)_5{=}GeCl_2$ and $W(CO)_5{=}Ge{=}W(CO)_5$: Electrochemical synthesis and quantum-chemical computations

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Abstract

Convenient synthetic route to prepare the germylene complexes of tungsten pentacarbonyls, $W(CO)_5{=}GeCl_2$ and $W(CO)_5{=}Ge{=}W(CO)_5$, electrochemically is developed. Combined quantum-chemical/IR spectroscopic approach is used for identification of the synthesized compounds. Good agreement between theoretical and experimental spectra can be regarded as one of the proofs of their supposed structures.

Keywords: Dichlorogermylene complex of tungsten pentacarbonyls; Germylenebis(tungsten pentacarbonyl) complex; Electrolysis; Cyclic voltammetry; Combined quantum-chemical/IR spectroscopic approach; Vibrational frequencies

1. Introduction

The chemistry of transition metals complexes has been studied extensively in last decade. In particular, the stabilization of short-lived intermediates of organic reactions by means of their coordination with transition metals is one of the focuses of modern synthetic chemistry. The studies of organometallic carbene analogues such as germylene, phosphinidene and silylene complexes are of special interest. The known procedure to obtain dichlorogermylene complexes of metal carbonyls includes the reaction of $GeCl_2 \cdot$ dioxane with photochemically generated species $(CO)_5M \cdot THF$ [1]. Germylene particles are generated by thermal or photochemical decomposition of suitable precursors [2], mainly by the thermal decomposition of 7-germanorbornadienes. Methods to obtain dichlorogermylene complexes of metal carbonyls on photochemical reaction of tungsten hexacarbonyl and $CsGeCl_3$ [3], and from $W_2(CO)_{10}$ and germanium tetrachloride [4] was reported also. The possibilities of the synthesis of germylene complexes using the electrochemical methods have not yet been explored.

An electrolysis and a cyclic voltammetry were used for germylene complexes of tungsten pentacarbonyl synthesis.

Previously it has been shown that an electrolysis of solution of tungsten hexacarbonyl **1** in acetonitrile (10^{-3} mol) in presence of Et_4NBF_4 as a supporting electrolyte after passing 2F per initial metal carbonyl yielded to highly nucleophilic anion of tungsten pentacarbonyl $[W(CO)_5]^{2-}$ **2** [5]:

$$\underset{\mathbf{1}}{W(CO)_6} \xrightarrow[-CO]{e} [\ W(CO)_5] \xrightarrow{e} [\ \underset{\mathbf{2}}{W(CO)_5}]^{2-} \quad (1)$$

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